Mixture Analysis by Membrane Introduction Mass Spectrometry

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Overview

Membrane Introduction Mass Spectrometery (MIMS) is a technique which can be used for rapid characterization of organic compounds in water. Because spectra of all compounds are acquired nearly simultaneously, significant problems can occur in the analysis of complex mixtures. Chemometric data analysis has been applied to MIMS data acquired from mixtures of aromatic compounds with similar and overlapping spectra (benzene, toluene, ethyl benzene and xylenes). Multivariate calibration techniques (partial least-squares, PLS) proved successful in predicting concentrations in mixtures where univariate methods failed.

Introduction

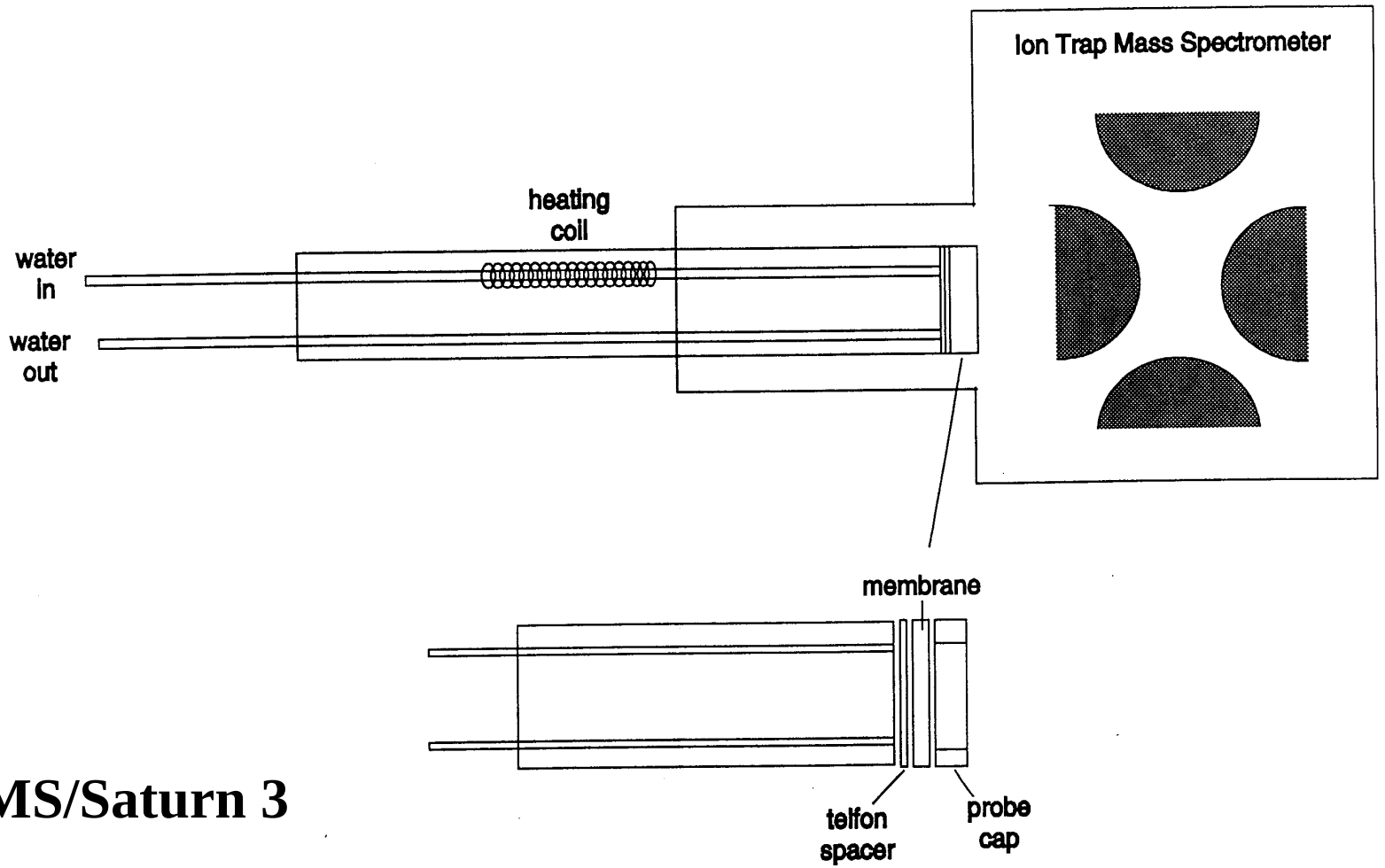
The simultaneous diffusion of compounds through the membrane in membrane introduction mass spectrometry (MIMS) is one of the method's principal strengths, in that all analytical information is acquired in a relatively short time. However, simultaneous introduction of a complex mixture into a mass spectrometer poses problems where there are not enough "pure" ions available for quantification and identification.

This poster presents the use of multivariate calibration for mixture analysis using MIMS. Multivariate calibration using partial least-squares (PLS) regression was used for the quantification and identification of three mixtures of increasing complexity.

Experimental

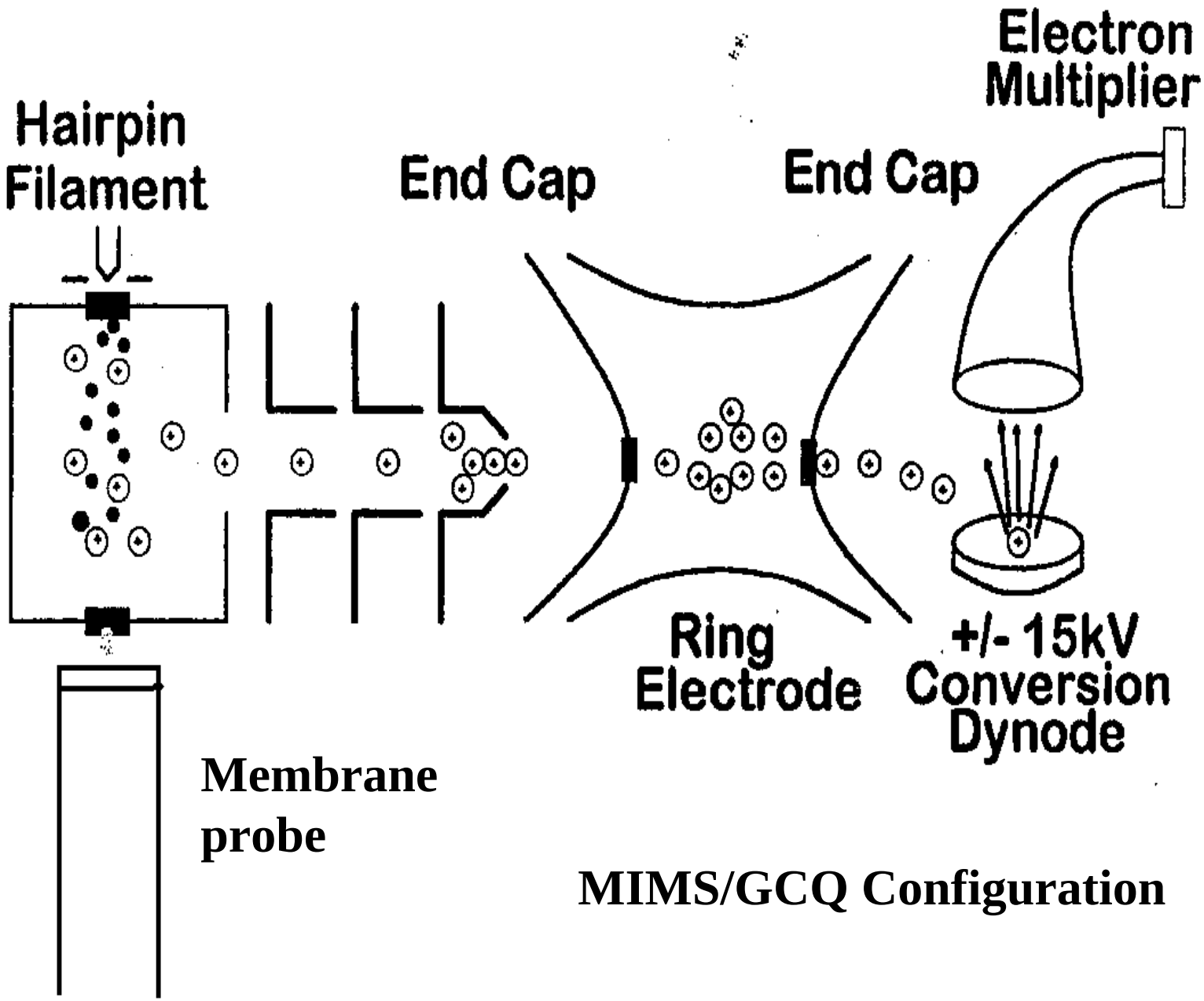
Membrane System :	Direct Insertion Probe MIMS Technology Inc. temperature: 50C flow: 1-2ml/min
Membrane:	Silicone Rubber Sheet Silastic, 0.01" thickness
Ion Trap MS:	Varian Saturn 3 GC/MS Finnigan MAT GCQ
Chemometrics:	MATLAB version 4.2c PLS_Toolbox 1.5.2

Direct Insertion Membrane Probe



MIMS/Saturn 3

Configuration



MIMS/GCQ Configuration

Multivariate Calibration

PLS regression consists of two steps:

(1) The data reduction step extracts features from the mass spectral data that correlate with analyte concentration, resulting in a PLS scores matrix ***(n x h***, where ***n*** is the number of spectra and ***h*** is the number of latent variables or PLS factors.)

(2) The multivariate calibration step that builds a model of the form

$$c_i = b_0 + b_1 x_{i,1} + ... + b_n x_{i,h}$$

where c_i is the predicted concentration for mass spectrum i, the x_i terms are the PLS factor scores, and the b terms are the regression coefficients.

Results and Discussion

Three mixtures of increasing complexity were analyzed:

1) A simple three-component mixture with minimal spectral overlap composed of benzene, toluene, and p-xylene (BTX),

2) A two-component isomer mixture of ethyl benzene and p-xylene (EX), and

3) A complex four-component mixture of benzene, toluene, p-xylene, and ethyl benzene (BTEX).

BTX Mixture

► BTX was analyzed for comparison between the multivariate and univariate calibration methods. A typical MIMS total ion current profile and mass spectrum is shown in Figures 1a & 1b.

► Correlation between the predicted concentrations from the PLS models and the actual concentrations are shown in Figure 2. Performance of the multivariate calibration methods is nearly identical to univariate models over the concentration range analyzed with prediction errors < 15% for univariate and < 13% for the multivariate calibration method. The multivariate calibration did not outperform the univariate method due to the limited calibration set used (10) and that little spectral interferences exists between the analytes.

Figure 1a

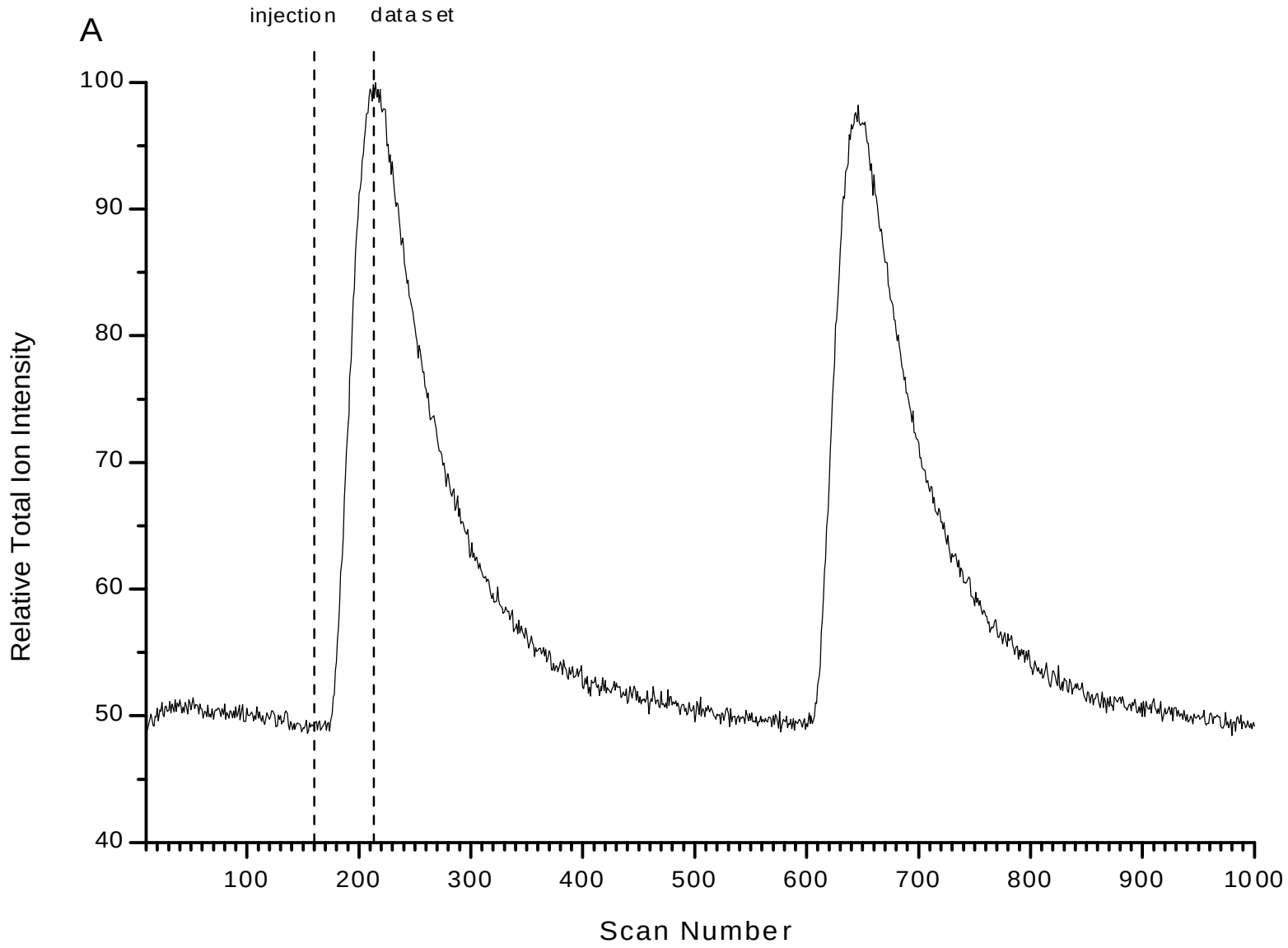

A
injection
data set
Relative Total Ion Intensity
100
90
80
70
60
50
40
100
200
300
400
500
600
700
800
900
1000
Scan Number

Figure 1b

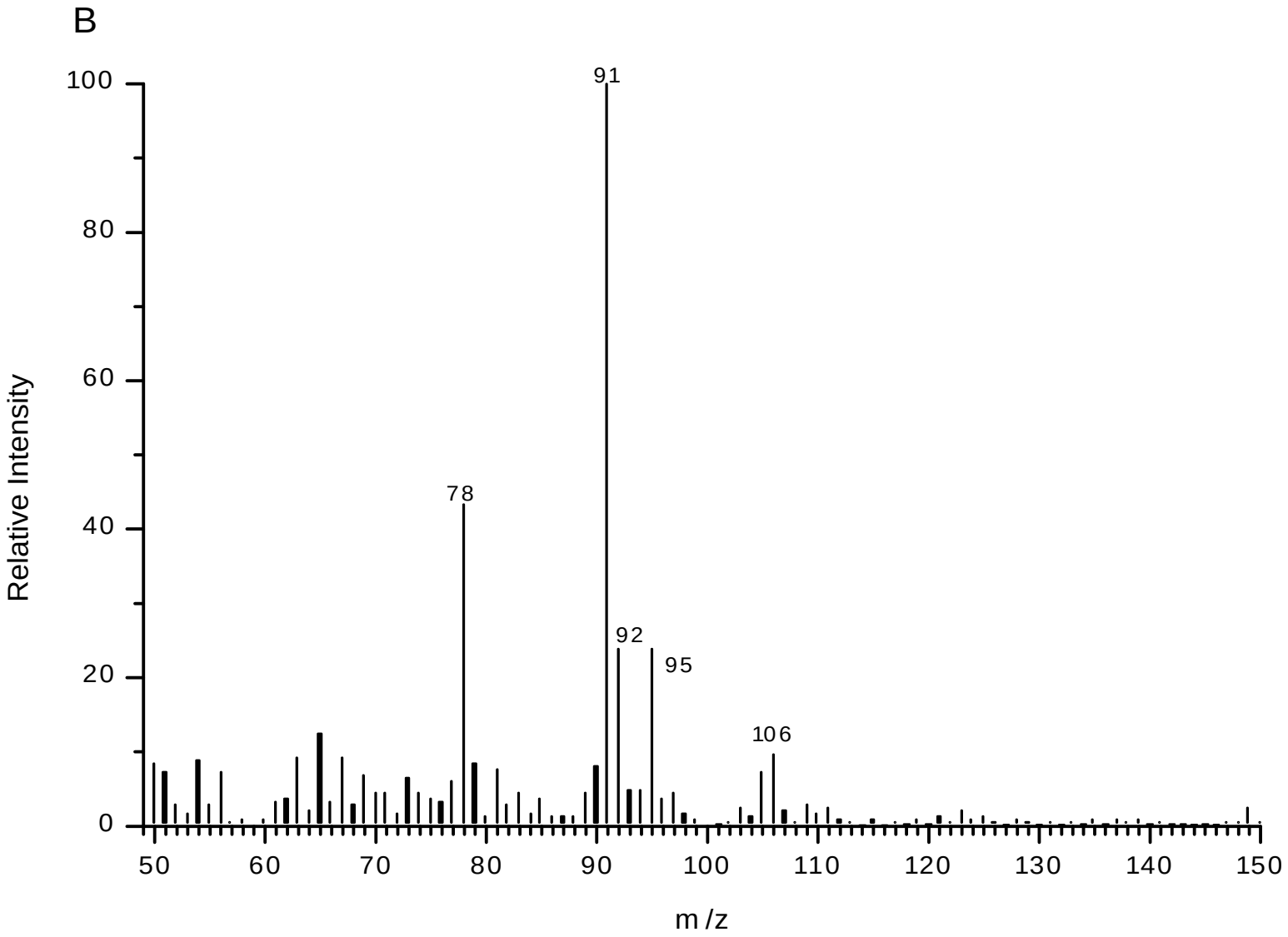
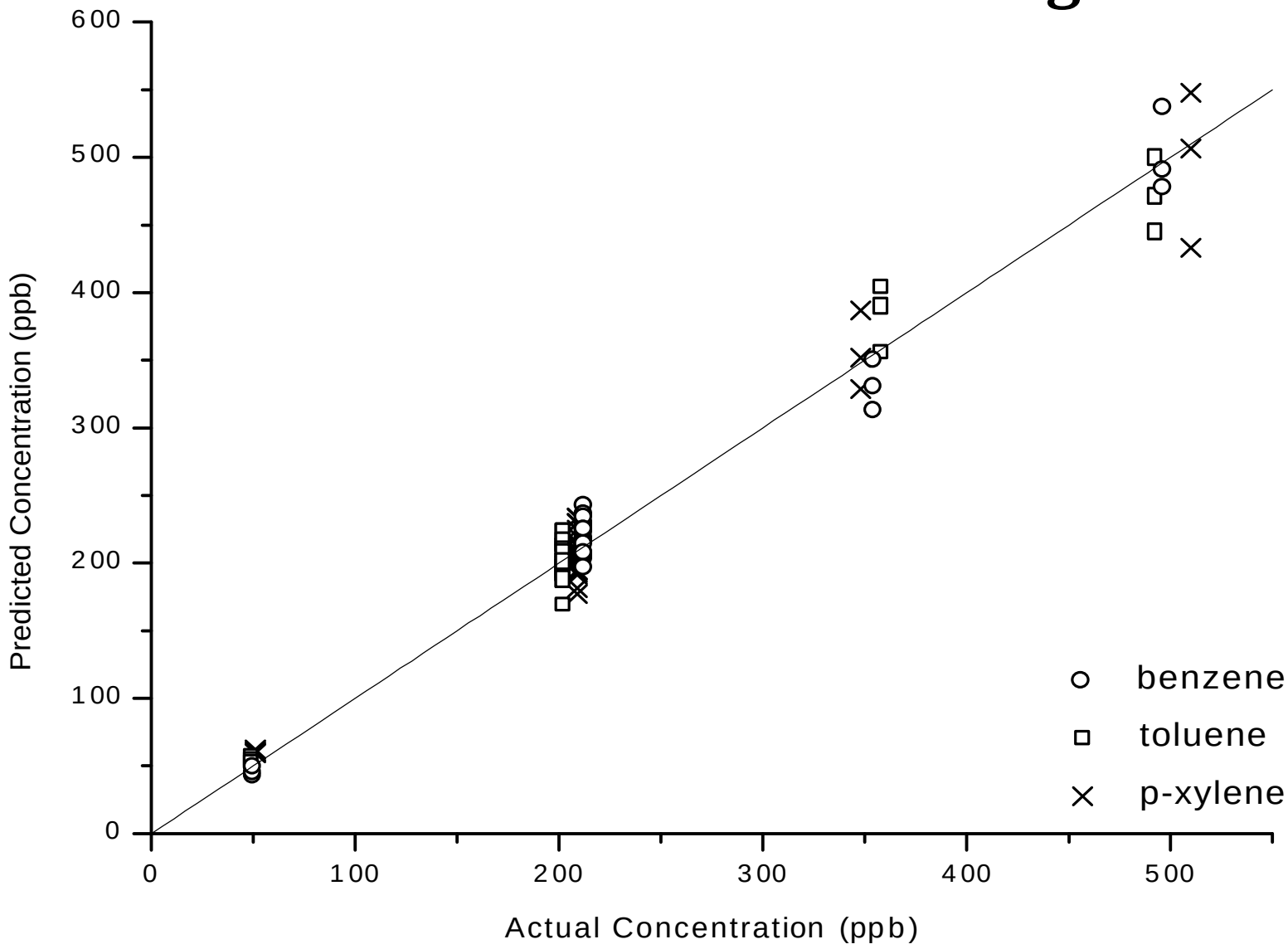

B
Relative Intensity
100
80
60
40
20
0
91
78
92
95
106
50
60
70
80
90
100
110
120
130
140
150
m/z

Figure 2


Predicted Concentration (ppb)
600
500
400
300
200
100
0
0
100
200
300
400
500
Actual Concentration (ppb)
benzene
toluene
p-xylene

EX Mixture

►The mass spectra of pure ethyl benzene and pure p-xylene (Figures 3A & 3B) are nearly identical and only differ by the ion abundances (Figure 3C).

► Using merely seven mixture samples, it was possible to build a multivariate calibration model with relative errors <12% (Figure 4). A univariate model was attempted using m/z 65 for ethyl benzene and m/z 105 for p-xylene (best responses found for linear regression) but little correlation between signal and concentration was found.

► A prinicipal component analysis (PCA) scores plot is shown in Figure 5. For the multivariate methods, such as PCA and PLS, distinct linear trends are observed for ethyl benzene and p-xylene. For the univariate method, no distinction was observed between the analytes.

Figure 3a

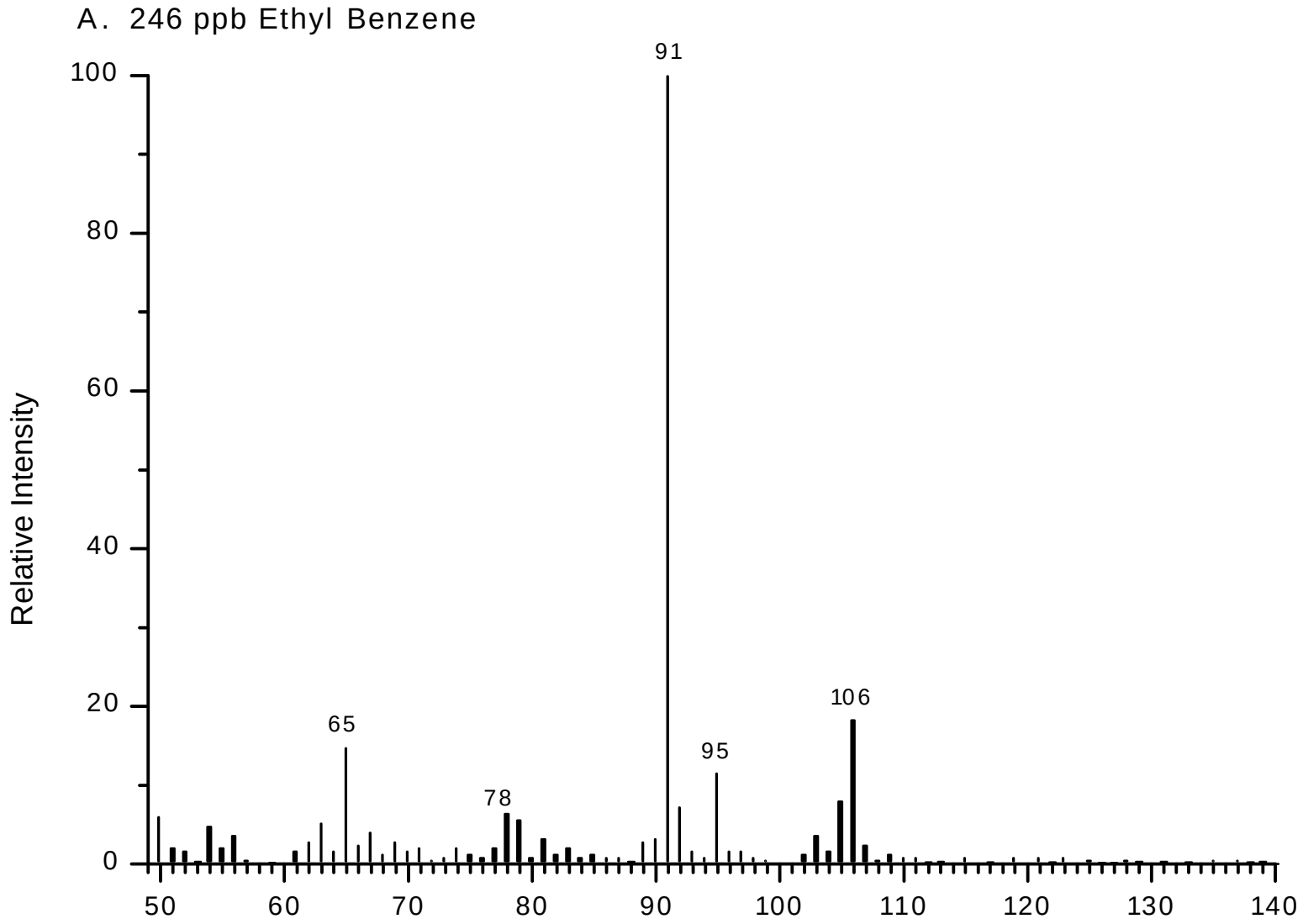

A. 246 ppb Ethyl Benzene
Relative Intensity
100
80
60
40
20
0
50
60
70
80
90
100
110
120
130
140
91
65
78
95
106

Figure 3b

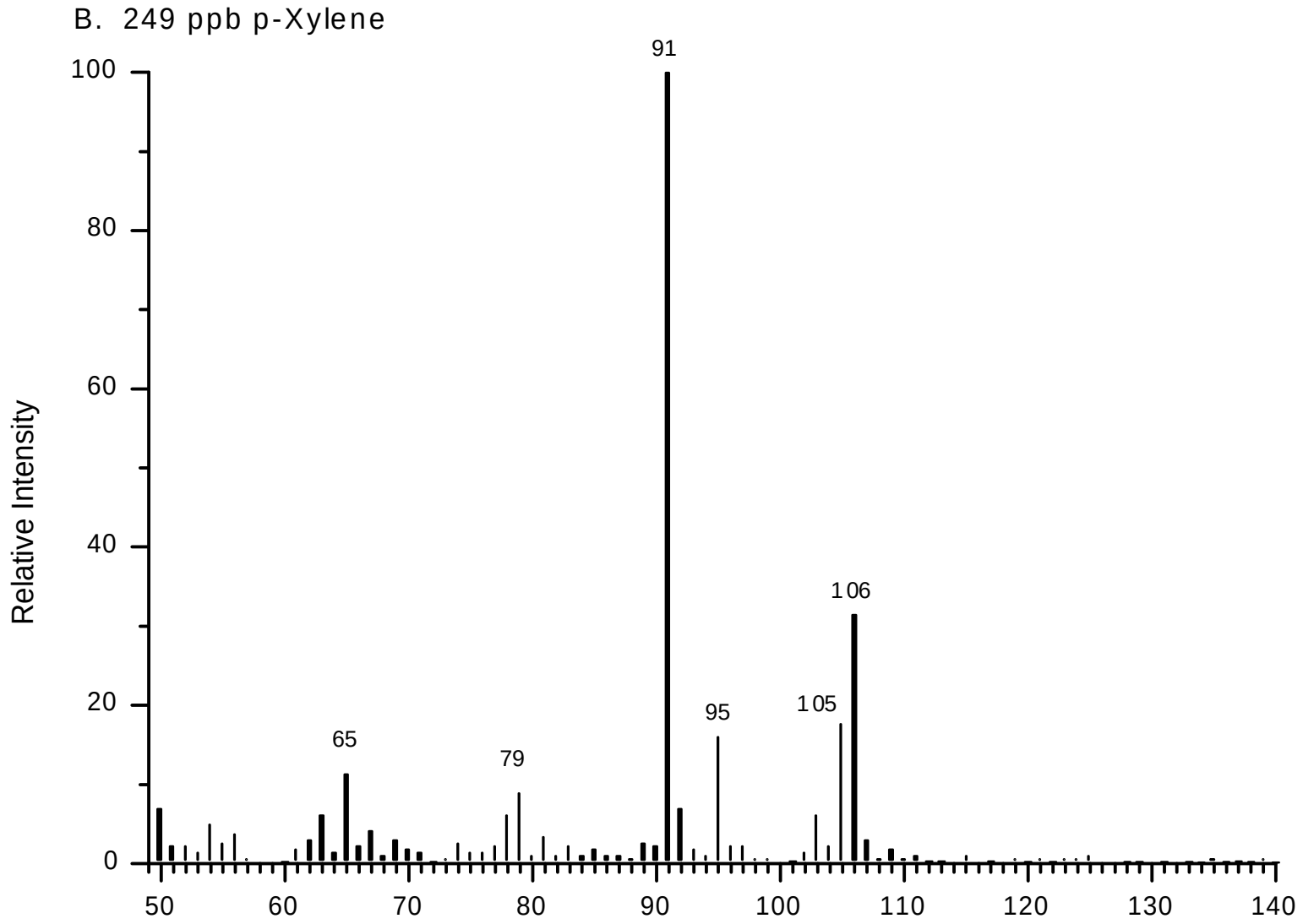

B. 249 ppb p-Xylene
Relative Intensity
100
80
60
40
20
0
50
60
70
80
90
100
110
120
130
140
91
106
105
95
65
79

Figure 3c

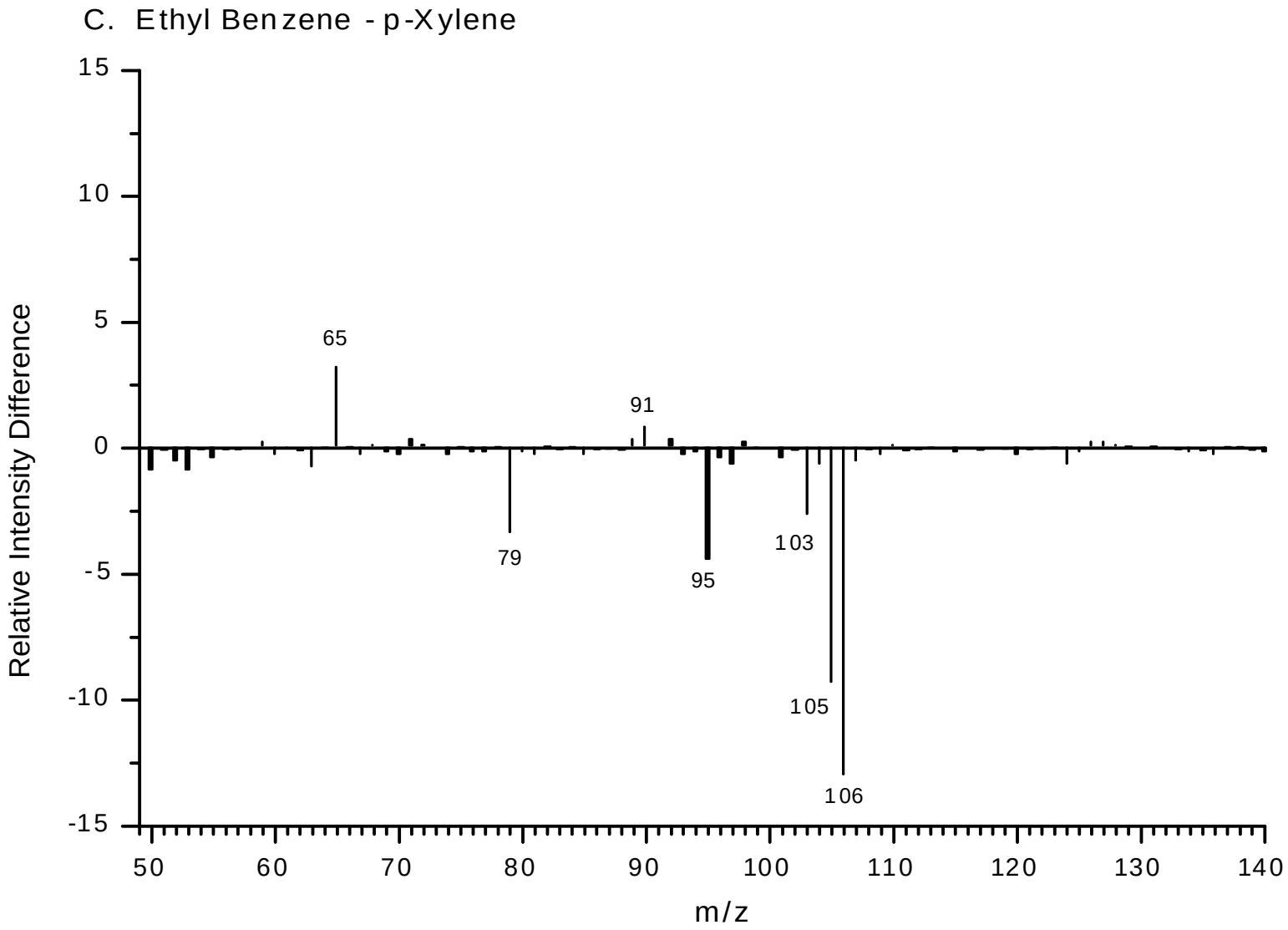

C. Ethyl Benzene - p-Xylene
Relative Intensity Difference
15
10
5
0
-5
-10
-15
65
91
79
95
103
105
106
50
60
70
80
90
100
110
120
130
140
m/z

Figure 4

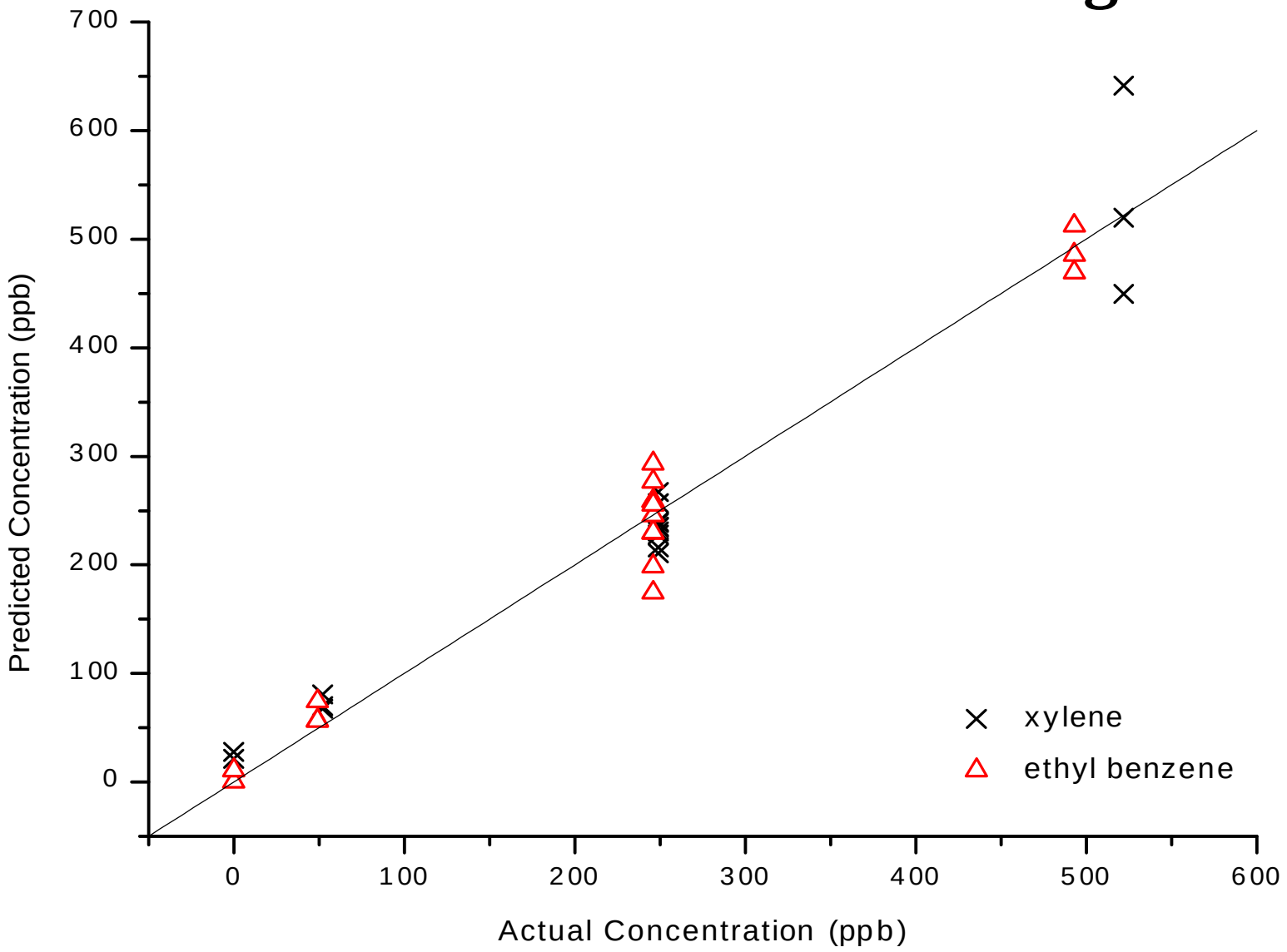
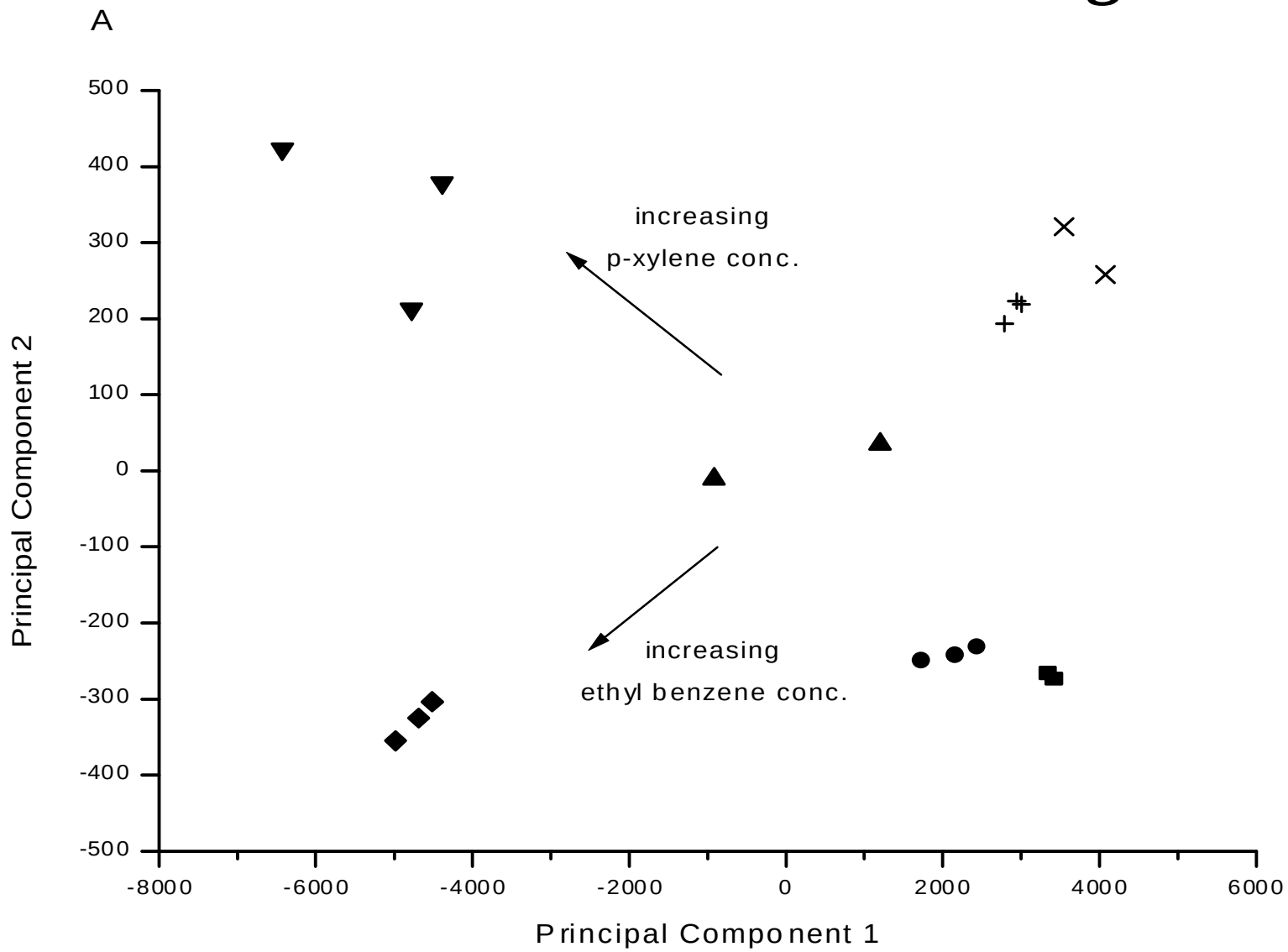

Predicted Concentration (ppb)
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
Actual Concentration (ppb)
xylene
ethyl benzene

Figure 5

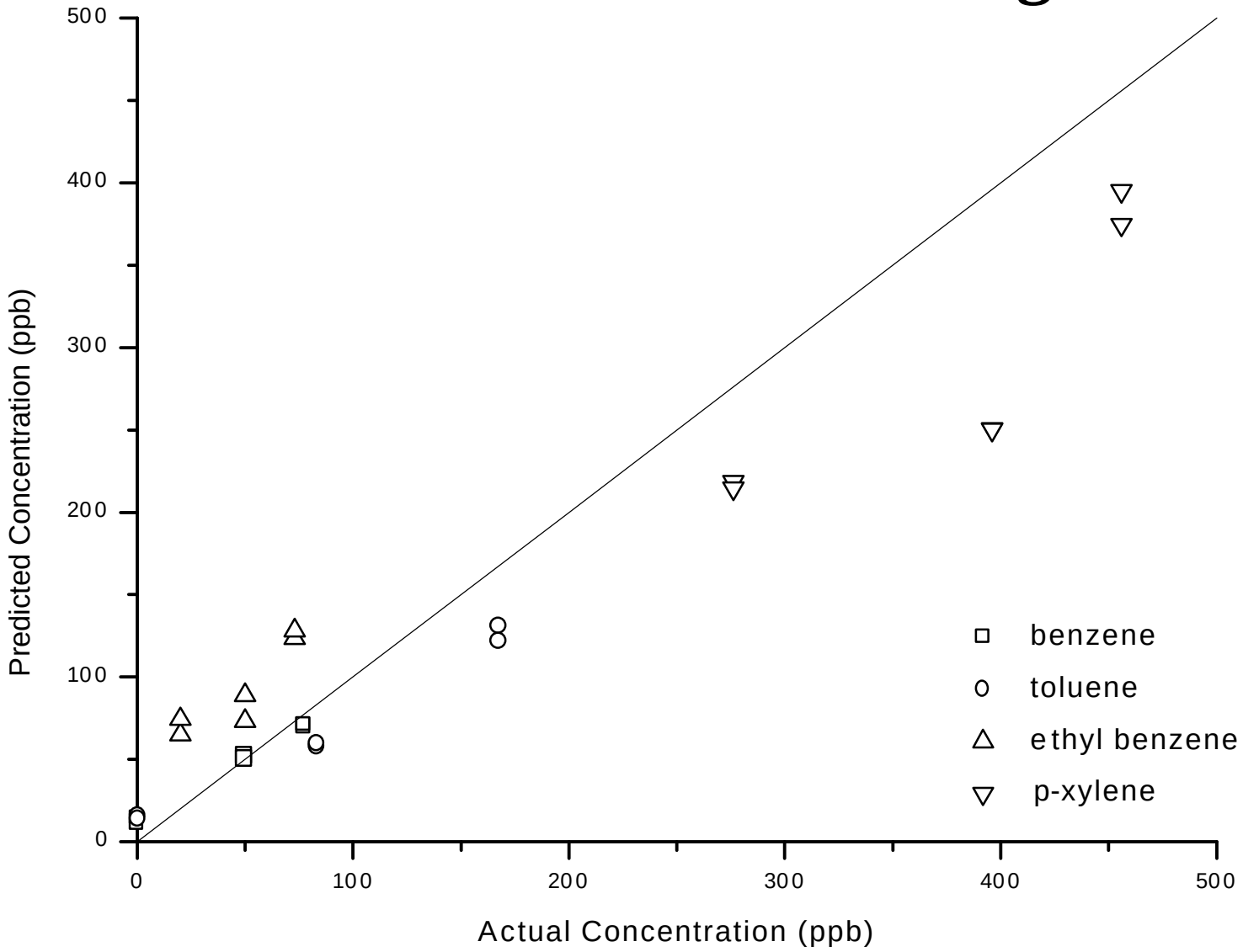

A
500
400
300
200
100
0
-100
-200
-300
-400
-500
Principal Component 2
-8000
-6000
-4000
-2000
0
2000
4000
6000
Principal Component 1
increasing
p-xylene conc.
increasing
ethyl benzene conc.

BTEX Mixture

► For the BTEX mixture, a larger sample set (24 mixtures) was designed to give the maximum amount of spectral information for the least amount of samples. While the test samples were chosen to represent known environmental samples of interest and extreme situations.

► The predicted *v*. actual concentrations are shown in Figure 6. The relative calibration errors are all <15%, while the prediction errors are <20% except for p-xylene. The large error for p-xylene can be attributed to a test sample containing a small quantity of ethyl benzene in the presence of a large quantity of p-xylene.

Figure 6


Predicted Concentration (ppb)
Actual Concentration (ppb)
0
100
200
300
400
500
benzene
toluene
ethyl benzene
p-xylene

Conclusions

► Using multivariate calibration, complex mixtures could be qualitatively and quantitatively analyzed for analytes having overlapping spectra.

► A mixture of isomers could be analyzed with prediction errors under 20% except for the extreme case where the isomers' concentration difference was large.

► All PLS models gave reliable determinations of BTEX mixtures.

Future Work

► The models were built using the mass spectra or average mass spectra corresponding to the maximum peak height of the flow injection profile. An additional dimension could be added to the model if the entire flow injection profile was included (i.e., spectra and time) using multi-way or second order calibration algorithms.

► Larger errors were observed for benzene than expected using the multivariate method and is probably due to the inclusion of minor noise ions in the model. Elimination of unimportant or noise ions could be accomplished by the judicious choice of ions to include in the model.

Acknowledgements

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